

Attempt to observe the direct interaction between Au-Au in the luminescent

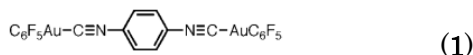
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1 Introduction

Reversible mechanochromism is the phenomenon of color change induced by mechanical grinding or pressing of a solid sample, and the subsequent reversion to its original color reversibly through treatment such as heating or recrystallization. Photoluminescent compounds that possess mechanochromic properties in their solid-state emissions can provide unique recording or sensing materials that involve luminescence detection. The mechanochromic luminescence behavior of $[(C_6F_5Au)_2(\mu-1,4\text{-diisocyanobenzene})]$ (1), has been reported as the photoluminescence of the solid, upon grinding, to undergo a drastic change and, upon exposure to solvent or its vapor, being restored to its original color.[1]



It was assumed that intermolecular aurophilic interactions were responsible for the altered emission of the ground samples. But direct evidence was hardly obtained because of its amorphous structure after the grinding. In this work we tried to elucidate the Au-Au interaction directly by the difference EXAFS method.

2 Experiment

The sample was prepared in a previously reported way.[1] The experiments were carried out in BL9A of Photon Factory. Au L_3 edge was measured at 15 K in order to reduce the thermal vibration of Au-Au bonding.

3 Results and Discussion

Figure 1 shows the EXAFS oscillations before and after the grinding process. There was no big difference, indicating the Au molecular structure was unchanged.

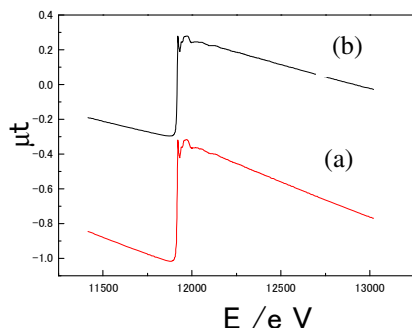


Fig.1 XAFS spectra of (1) before (a) and after (b) grinding.

We carried out the difference spectrum analysis between the two. Figs. 2 and 3 show the difference

EXAFS spectrum and its Fourier transform, respectively. A small oscillation appeared in Fig.2 which was Fourier transformed to give a peak at 2.5 Å. We performed the curve fitting analysis assuming the peak might appear with the Au-Au interaction and found 0.36 Au was present at 3.17 Å. However, the peak was very small and more careful investigations such as checking the reproducibility and measuring the other similar samples which show mechanochromism are necessary as well as the measurement of the sample at much lower temperature (around 4 K).

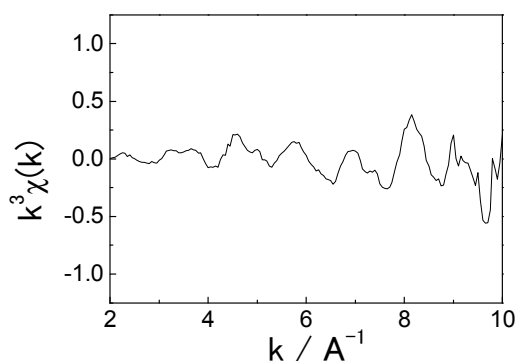


Fig.2 A difference spectrum between the ones after and before the grinding sample measured at 15 K.

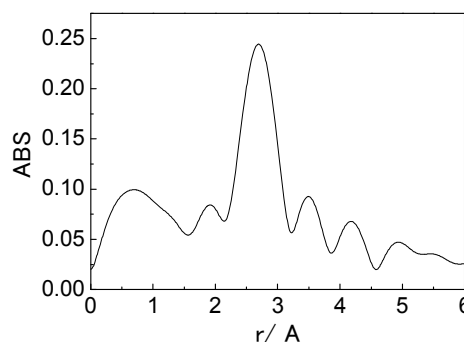


Fig.3 Fourier transform of the difference spectrum in Fig.2.

[1] H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, *J. Am. Chem. Soc.* 2008, **130**, 10044.

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